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DEPOLARIZED RAYLEIGH SCATTERING AND ORIENTATIONAL MOTION OF POL--ETC(U)

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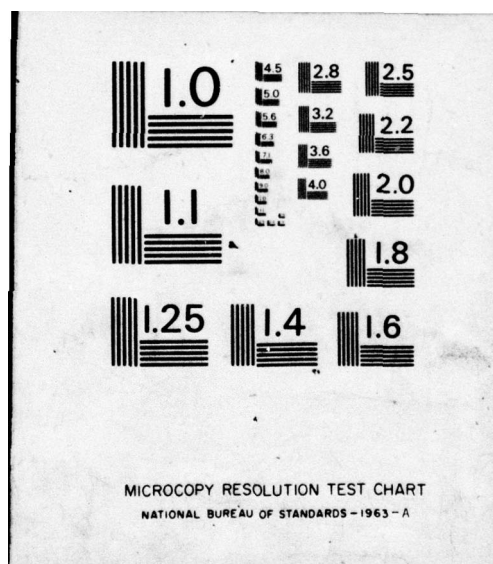
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Depolarized Rayleigh Scattering
and Orientational Motion of
Polyethylene Glycol

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Abstract

The depolarized Rayleigh light scattering spectra of pure polyethylene glycols and their solutions in an optically isotropic solvent were studied as a function of polymer molecular weight, concentration and temperature. Reorientational relaxation times were obtained by fitting the observed spectra to Lorentzian functions convoluted with the experimental spectrum. The relaxation times were found to increase with increasing molecular weight and with dilution. The depolarized Rayleigh results for the polyethylene glycols were compared with results for other polymer systems and with results obtained using other types of relaxation studies. By studying the dependence of the relaxation times on viscosity, temperature and concentration and comparing the results with theoretical predictions of molecular and end-group reorientations, we have associated the depolarized Rayleigh spectra of polyethylene glycol with rotation of the entire polymer molecule.

I. Introduction

Dielectric relaxation, nuclear magnetic resonance spin-lattice relaxation and neutron scattering can yield information on the orientational motion of polymers in the liquid state. In a previous work, it was shown that polarized Brillouin - Rayleigh scattering could be used to determine the effects of density fluctuations in pure polymers.¹

Depolarized Rayleigh light scattering could also be used to study molecular motion of polymer melts and solutions. The mechanisms for depolarized Rayleigh scattering are density fluctuations and anisotropy fluctuations, as both can modulate the Rayleigh polarizability tensor. However, depolarized Rayleigh scattering due to density fluctuations is small relative to the anisotropy fluctuations, and in most cases an unambiguous separation of density and anisotropic effects can be obtained.

Depolarized Rayleigh scattering spectra have been measured for several small molecules by Pecora and co-workers² and in this laboratory³. It has been found that the depolarized spectra of small molecules are primarily determined by overall molecular rotational motion. Therefore, we expect that the spectra of polymers in solution might also be dependent on overall rotational motion.

In a previous paper⁴ (hereafter referred to as I), we demonstrated how depolarized Rayleigh scattering could be used to study the segmental motion in pure polypropylene glycols. In polymers, at least three different types of motions can give rise to depolarized Rayleigh scattering. The first type of motion is rotation of the entire molecule. For a dilute solution of relatively small cylindrically symmetric polymer molecules, the depolarized Rayleigh spectrum is a single Lorentzian with half-width at half-height (HWHH) given by⁵

$$\Gamma = \left(\frac{1}{2\pi}\right) 6 D_R \quad (1)$$

where Γ is the HWHH in Hz and D_R is the rotational diffusion coefficient. For asymmetric molecules, the molecular reorientational spectrum becomes the sum of as many as five Lorentzians. The depolarized Rayleigh relaxation time, τ_{Ray} , is related to the HWHH of the experimental Lorentzian spectrum by

$$\tau_{\text{Ray}} = (2\pi\Gamma)^{-1} \quad (2)$$

In contrast to Raman scattering, depolarized Rayleigh spectral power density for concentrated solutions of scattering molecules depends on both single particle motions and static and dynamic correlated motions of molecular pairs. In concentrated solutions pair correlations may become important⁶ and the measured relaxation time, τ_{Ray} , is related to the single particle relaxation time, τ_s , by⁶

$$\tau_{\text{Ray}} = \tau_s \left(\frac{1+fn}{1+gn} \right) \quad (3)$$

where f and g measure the strength of static and dynamic pair correlations and n is the number density of the scatterers.

A second form of orientational motion in polymers which can give rise to depolarized Rayleigh scattering is the internal rotation of end groups or of unhindered side chains. This orientational motion is also characterized by a single relaxation time for orientational motion of a given cylindrically symmetric group and could also show effects due to pair correlations. In general, this relaxation time should be much shorter than the reorientation time for the entire molecule since it is expected that small groups will reorient very quickly.

Polymers can undergo a third type of motion through local movements of polymer segments (not the collective motion of the Rouse-Zimm type⁷). As we have discussed in I, this polymer backbone motion can give rise to depolarized Rayleigh scattering through two mechanisms: segmental reorientation and seg-

mental center of mass motion. The segmental center of mass motion which is the dominant mechanism for the polarized Brillouin scattering contributes to the depolarized Rayleigh scattering spectrum because the polarizability anisotropy of the segment depends on position.

The three types of motion are expected to have different concentration dependences. Polymer molecules generally expand in solution due to the excluded volume effect and solvent-solute interaction⁸. Thus, when viscosity and temperature effects are taken into account, the reorientation of the entire polymer molecule should become slower as the polymer concentration is decreased. On the other hand, the concentration effects on simple end groups and unhindered side chains should be small. However, if strong inter-group forces (e.g. hydrogen bonding) are present, the concentration effects could be fairly large and should depend on such factors as solvent and the presence of intramolecular interactions. Local backbone segmental motion is also expected to become slower as the polymer concentration is decreased since larger segments of the backbone are free to move as the polymer swells with dilution.

The molecular weight (or degree of polymerization) of the polymer can affect the Rayleigh relaxation time. The rotation of the entire molecule should be significantly slower for higher molecular weight samples of the same polymer. On the other hand, the end group or side chain reorientations and the backbone segmental motion will show little change with molecular weight.

We used these ideas in I to analyze the depolarized Rayleigh scattering spectra from a series of polypropylene glycols ranging in molecular weight from 425 to 4000. In this work, we report results of depolarized Rayleigh light scattering study of polyethylene glycols $[\text{H}-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}]$ as a function of molecular weight, concentration and temperature. The relaxation times obtained from the depolarized Rayleigh spectra are analyzed in light

of the above discussion in an attempt to relate the times to the various possible relaxation processes in this system of polymers.

II. Experimental

The depolarized Rayleigh spectra were taken using the apparatus described in I. The single mode incident laser output at 488.0 nm ranged from 0.3 to 0.5 W. All spectra were obtained using a 90° scattering angle with the incident light polarized perpendicular to the scattering plane and the scattered light polarized parallel to the scattering plane. The scattered light was analyzed using a piezoelectrically scanned Fabry-Perot interferometer fitted with plane mirrors. For the spectra reported here, plate separations ranging from 0.989 to 5.46 cm were used, corresponding to free spectral ranges between 15.2 and 2.74 GHz. The total instrumental finesse ranged from over 70 at the smaller plate separations to 35 at the larger separations. The frequency analyzed light was amplified by a cooled photomultiplier and picoammeter. The resulting signal was displayed on X-Y recorder. The instrumental profile (laser plus interferometer and collection optics) was measured at each plate separation and was found to be fitted well by a Voigt function⁹. After correction for the instrumental contribution and the overlap of adjacent orders, all spectra were found to fit well by a single Lorentzian. There is no indication of a depolarized Brillouin doublet or spectral dip at the line center in any of the liquids studied.⁶ The Brillouin spectra measured in the polarized scattering geometry for the pure samples were also obtained as a function of temperature and will be reported elsewhere.

The polyethylene glycol (PEG) samples having average molecular weights of 200 and 400 were obtained from Polysciences, Inc., Warrington PA. Triethylene glycol was obtained from Aldrich Chemical Company, Inc., Milwaukee WI. A 50/50 by volume mixture of carbon tetrachloride and tert-

butyl alcohol was used as a solvent for the solution studied. The depolarized Rayleigh scattering from this solvent was measured and was found to contribute negligibly to the total sample-solvent scattering intensity. The samples were filtered through 0.22 μm Millipore filters into rectangular glass cells. The cell was placed in a brass holder, the temperature of which was controlled with a water-ethylene glycol solution circulated by a Haake FK-2 bath. The temperature is accurate to better than ± 1 K. Kinematic viscosities and densities of the samples studied were measured using Cannon-Ubbelohde viscometers and a calibrated pycnometer thermostated in a temperature bath. The absolute viscosities are accurate to better than $\pm 5\%$.

III. Results and Discussion

Depolarized Rayleigh light scattering spectra were obtained for pure PEG 200 and solutions of triethylene glycol, PEG 200 and PEG 400 in a 50/50 by volume mixture of carbon tetrachloride and tert-butyl alcohol as a function of temperature. Depolarized Rayleigh relaxation times, τ_{Ray} , were obtained from the HWHH of the Lorentzian spectra using Eq. (2). These relaxation times were reproducible to better than 15%. The results of this study, along with the dielectric relaxation times, τ_{DI} , of pure ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol (PEG 200) obtained by Koizumi¹⁰ are presented in Table I. Pinnow, Candau and Litovitz¹¹ have obtained depolarized Rayleigh spectra for pure ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol. They fitted their data for each compound to an Arrhenius equation of the form

$$\tau_{\text{Ray}} = A \exp (E_a/RT). \quad (4)$$

Using their A and E_a values, we calculated τ_{Ray} values for these compounds. These values are included in Table I. The viscosities of all solutions studied were

also measured and are given in Table I.

Our τ_{Ray} values for a given concentration of a given molecular weight polymer could also be fitted by Eq. (4) and the results are plotted in Fig. 1 along with the results of Pinnow, *et al.* for pure triethylene glycol. The τ_{Ray} values for pure PEG 200 are significantly larger than those reported by Pinnow, *et al.*,¹¹ despite the fact that our measured τ_{Ray} values for pure diethylene glycol are in good agreement with their. We are at present unable to explain the difference in τ_{Ray} values for PEG 200 except pointing out that significantly larger Fabry-Perot plate separations have to be used for the study of pure PEG 200 than for the diethylene and triethylene glycol in order to resolve the depolarized Rayleigh component and enable the instrumental width to be properly corrected. At such large separations, great care was also needed to insure that the laser remained in a single mode for the duration of an experiment. We believe that our results represent better τ_{Ray} values for PEG 200.

The τ_{DI} values for the four pure compounds can be compared with the τ_{Ray} values. At infinite dilution (i.e. for single particle motion), the dielectric and depolarized Rayleigh rotational relaxation times for an overall molecular reorientation process occurring by small angular step rotational diffusion are related by $\tau_{\text{DI}} = 3 \tau_{\text{Ray}}$. A detailed discussion of the mechanism of molecular orientational relaxation required for this limiting relationship for the diffusion or jump process was given by Pinnow, *et al.*¹¹.

It should be pointed out that this relationship is not necessarily valid for concentrated solutions since dielectric relaxation and depolarized Rayleigh scattering have very different pair correlation effects⁶ and concentration dependences. Another possibility for $\tau_{\text{DI}} \neq 3 \tau_{\text{Ray}}$ is that the dielectric relaxation and depolarized Rayleigh scattering do not probe the same motion. In this case, there would be no limiting relationship between τ_{DI} and τ_{Ray} . As is clear from the values given for pure compounds in Table I, the value of

τ_{Ray} is nearly always larger than that of τ_{DI} , in disagreement with the prediction based upon the simple rotational diffusion model. It is also clear from Table I that the values of τ_{Ray} decrease with decreasing polymer concentration. This result can be understood in terms of the effect of solution viscosity, as to be discussed below.

The activation energy data for solutions are the new results. Our E_a value for pure PEG 200 is 7.0 Kcal/mole, which is about 3 Kcal/mole less than the value reported by Pinnow, *et al.*¹¹ We are unable to explain this difference, except again pointing out the difficulty of measuring the τ_{Ray} value for PEG 200 and higher molecular weight polymers using the interferometric technique. It is also interesting to point out that our E_a value is in good agreement with the spin-lattice relaxation result.¹³ The spin-lattice relaxation, inelastic neutron scattering¹⁴ and depolarized Rayleigh scattering in general probe similar types of molecular motion.

Activation energies obtained from the plots in Fig. 1 along with E_a values obtained by Koizumi¹⁰ and Pinnow, *et al.*¹¹ are given in Table II. More discussion of the significance of these activation energies will be given shortly.

Orientational relaxation times can often be described by a Stokes-Einstein type equation of the form^{2,3}

$$\tau = C \frac{\eta}{T} + \tau_0 \quad (5)$$

where η is the solution viscosity, T the absolute temperature and the constant C is determined by the size and shape of the particle, boundary conditions at the surface of the orienting particle and other molecular constants. This linear dependence of reorientation time on η/T has been observed experimentally in many liquid systems.^{2,3,12} In order to better characterize our relaxation times, we have plotted τ_{Ray} versus η/T for the samples. The results are shown in Figs. 2-5. Linear least squares fits of the data to Eq. (5) are also shown.

The fitted values of the slopes C and intercepts τ_0 are given in Table III. Also given are the values of C and τ_0 obtained from the dielectric relaxation data of Koizumi¹⁰ and the depolarized Rayleigh data of Pinnow *et al.*¹¹ Koizumi suggests that the τ values for ethylene glycol reflect motion of the whole molecule and that the large τ_{DI} values for diethylene glycol may be attributable to a ring structure of the molecule. For the higher oligomers, the orientation of the end OH groups is believed to be the largest contributor to the dipolar polarization. This interpretation is fairly consistent with the slopes from the τ_{DI} versus η/T plots. For ethylene and diethylene glycol, the slopes are the same and the E_a values from Table II are fairly close. Thus, the dielectric relaxation measurements are probing similar motions in these two molecules and the reorienting units have similar molecular dimensions. The overall length of ethylene glycol is comparable to the length of the diethylene glycol ring structure. For dielectric relaxation data, the triethylene and tetraethylene glycol slopes C are smaller but the activation energies are still ~ 8 kcal/mole. For these molecules, dielectric relaxation is probing the motion of a smaller unit, such as $-\text{OH}$ or $-\text{CH}_2\text{OH}$, and not rotation of the entire molecule. Since the E_a values for the four homologs are nearly the same, it is possible that they all have the same rate determining step (e.g. rotation of an $-\text{OH}$ or $-\text{CH}_2\text{OH}$).

The τ_{Ray} values for the pure compounds increase monotonically with increasing molecular weight, in contrast to the τ_{DI} data. The τ_{Ray} values for the pure compounds are plotted versus η/T in Fig. 2. The slopes from this plot show a different behavior than the dielectric data. For ethylene and diethylene glycol, the depolarized Rayleigh slopes are the same and are smaller than the corresponding dielectric relaxation slopes. However, as the molecular weight increases further, the depolarized Rayleigh slopes increase significantly suggesting that the size of the rotating unit is increasing with molecular weight.

This is in contrast to our results in I for poly-propylene glycols (PPG). For PPG, the slope of the τ_{Ray} versus η/T line was independent of molecular weight but the slope for more dilute solutions was greater than that for the more concentrated solutions. The depolarized Rayleigh scattering from PPG was associated with segmental motion of the polymer backbone. The increase in relaxation time with dilution was a result of the polymer swelling, allowing larger segments to move freely.⁴

In the case of PEG, the Rayleigh relaxation time data show a strong molecular weight dependence, and asymptotic behavior of τ_{Ray} is reached slowly. Anderson, et al.¹⁵ have measured the spin-lattice relaxation time of PEG as a function of molecular weight, and have shown that the relaxation time becomes insensitive only when the degree of polymerization is 30 or greater. That is when the molecular weight of PEG is about 1500 or greater. Although we do not imply the same situation to occur in light scattering, it is reasonable to expect that τ_{Ray} will become molecular weight dependent at about the same molecular weight range. For the present Rayleigh scattering experiment, we were unable to measure accurate τ_{Ray} values even for pure PEG 400 at any Fabry-Perot plate separation due to the extremely small linewidth associated with orientational motion of the highly viscous polymer. The mechanism of backbone segmental motion which is responsible for the depolarized Rayleigh scattering of PPG is also expected in PEG. However, the observed spectra were not successful. This, thus, indicates either that the backbone segmental motion of PEG does not change the Rayleigh polarizability anisotropy significantly or that the backbone motion is too slow to be resolved by the Fabry-Perot interferometric technique. Because of the unusual helical configuration of PEG,¹⁴ it is likely that the second reason is applicable.

From Figs. 3-5 it is seen that for each system whose concentration dependence was studied, the relaxation times for the more dilute solutions show a stronger η/T dependence than the times for the concentrated solutions and pure polymer.

This result can be explained in terms of the expansion of the polymer molecule upon dilution. We have calculated volumes for the rotating units from the experimental C values using

$$C = \frac{V}{k} \quad (6)$$

where V is the volume of the rotating particle and k is Boltzmann's constant. This formulation assumes "stick" boundary conditions, where fluid adjacent to the rotating particle sticks to the particle and rotates with it. These volumes are included in Tabel III. It is realized these volumes are at best only order of magnitude values, but they should give some insight as to the size of the rotating particle. It is clear these volumes are too large to be associated with end groups, such as $-OH$ or $-CH_2OH$. Also, these volumes increase as the degree of polymerization increases, suggesting segmental reorientation is not responsible for the depolarized Rayleigh scattering. The values are consistent, however, if the scattering is interpreted as resulting from rotation of the entire molecule. Also as predicted according to this mechanism, the total molecular volume increases both with increasing molecular weight and with dilution because of the solute-solvent interaction and the excluded volume effect.

The intercepts of the τ versus η/T plots also give information about the rotational motion being investigated. In I, positive non-zero intercepts were obtained for PPG. Thus, the relaxation time is finite at zero viscosity (or infinite temperature). This is reasonable for polymer backbone segmental motion since the segments are bonded to one another and are restricted in their motion even at zero viscosity. The PEG plots shown in Figs. 2-5 all have zero intercepts within the experimental uncertainty. This is consistent with our interpretation of depolarized Rayleigh scattering in these molecules occurring as a result of rotation of the entire molecule.

The activation energies for molecular reorientation obtained from the depolarized Rayleigh experiments agree well with each other and with the dielectric relaxation results (the uncertainties in the E_a values are of the order of 10%) but are significantly larger than values obtained for rotation of lower viscosity liquids composed of small molecules.^{2,3} The depolarized Rayleigh E_a value for diethylene glycol is somewhat low. Allen, Connor and Pursey¹³ have studied PEG using nuclear magnetic resonance spin-lattice relaxation. E_a values from their $\log T_1$ versus T^{-1} plots were 7 kcal/mole for diethylene glycol, triethylene glycol and PEG 200. Again these E_a values agree well with those obtained using other techniques suggesting all of the orientational motions involve the same type of process. It is likely this process involves the breaking of hydrogen bonds as it is necessary for hydrogen bonds to be broken both for the movement of end groups and for rotation of the molecule as a whole.

IV. Conclusions

In conclusion, it should be emphasized that although these polyethylene glycols are capable of undergoing several types of orientational motion, only one relaxation time was observed. End group and backbone motion possible give some small contribution to the scattering spectrum but, as is shown above, an interpretation based on rotation of the entire molecule is consistent with the experimental results.

In summary we have studied depolarized Rayleigh scattering spectra of a series of polyethylene glycol solutions as a function of molecular weight, concentration and temperature. The solvent used in this work was a mixture of carbon tetrachloride and tert-butyl alcohol which has negligible depolarized scattering of its own. The relaxation times were obtained by fitting the observed spectra to Lorentzian functions convoluted with the instrumental spectrum. By studying the dependence of the relaxation times on viscosity, concentration and temperature

and comparing the results with theoretical predictions of molecular and end-group reorientations, we have concluded that rotation of the entire polymer molecule is responsible for the depolarized Rayleigh scattering in PEG solutions. This conclusion was reached by examining the various reorientational motions which could possibly contribute to depolarized Rayleigh scattering in these molecules. The relaxation times were found to increase with increasing molecular weight and with dilution. The present results were compared with dielectric relaxation times and other spectroscopic studies. The activation energies observed in depolarized Rayleigh scattering are consistent with those obtained using other techniques.

Acknowledgement

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TABLE I

Orientational Relaxation times

14

Sample	T/K	$\tau_{\text{Ray}}/\text{ns}^a$	$\tau_{\text{DI}}/\text{ns}^b$	η/cp
PEG 400, 21 mole%	275.5	3.2		48.2
	280.8	2.6		35.6
	288.2	0.96		24.0
	293.7	0.88		18.6
	298.4	0.77		15.0
	306.9	0.63		10.5
	319.2	0.47		6.84
	327.2	0.35		5.22
PEG 400, 35 mole%	298.0	1.35		27.5
	307.2	0.98		18.2
	314.6	0.77		13.6
	320.2	0.61		11.3
	326.8	0.46		9.2
	333.2	0.42		7.6
PEG 200, pure	278.2		0.53	175
	293.2	1.41 ^c	0.23	68.5
	302.7	1.34		40.5
	308.2	0.60 ^c	0.114	32.0
	312.7	0.77		26.5
	320.7	0.68		19.2
	323.2	0.28 ^c	0.066	17.7
	333.7	0.40		12.6
	339.7	0.375		10.5
PEG 200, 35 mole%	283.4	1.27		28.2
	289.6	0.84		20.5
	293.7	0.77		17.5
	302.8	0.47		11.7
	311.7	0.30		8.6
Triethylene glycol, pure	278.2		0.55	119
	293.2	0.78 ^c	0.24	99.5
	308.2	0.39 ^c	0.12	22.7
	323.2	0.21 ^c	0.066	130.0
	353.2	0.070 ^c		5.4
Triethylene glycol, 35 mole%	289.0	.359		11.8
	294.8	.262		9.25
	301.3	.211		7.10
	306.7	.188		5.85
	316.8	.127		4.25
Diethylene glycol, pure	278.2		0.72	88
	293.2	0.24 ^c	0.28	36.8
	308.2	0.15 ^c	0.145	18
	323.2	0.10 ^c	0.069	10.3
	353.2	0.052 ^c		4.35
Ethylene glycol, pure	278.2		0.34	44.5
	293.2	0.093 ^c	0.13	20.7
	308.2	0.040 ^c	0.072	11.5
	323.2	0.019 ^c	0.044	6.9
	353.2	0.005 ^c		3.2

a. this work unless otherwise noted.

b. all dielectric times are from Ref. 10.

c. Ref. 11.

TABLE II
Orientational Activation Energies

<u>System</u>	<u>Type of Experiment</u>	<u>E_a/kcal mole⁻¹</u>
PEG 400, 35 mole%	depolarized Rayleigh ^a	6.8
PEG 400, 21 mole%	depolarized Rayleigh ^a	7.3
PEG 200, pure	depolarized Rayleigh ^a	7.0
	depolarized Rayleigh ^b	10.2
	dielectric relaxation ^c	8.3
	spin-lattice relaxation ^d	~7
PEG 200, 35 mole%	depolarized Rayleigh ^a	8.8
Triethylene glycol, pure	depolarized Rayleigh ^b	8.3
	dielectric relaxation ^c	8.3
	spin-lattice relaxation ^d	~7
Triethylene glycol, 35 mole%	depolarized Rayleigh ^a	6.5
Diethylene glycol, pure	depolarized Rayleigh ^b	5.2
	dielectric relaxation ^c	8.8
	spin-lattice relaxation ^d	~7
	depolarized Rayleigh ^b	10.0
Ethylene glycol, pure	dielectric relaxation ^c	8.0

a) this work

b) Ref. 11

c) Ref. 10

d) Ref. 13

TABLE III

Experimental Viscosity Dependences

<u>System</u>	<u>Type of Experiment</u>	<u>Slope $\frac{C}{\eta s \text{ K cp}^{-1}}$</u>	<u>Intercept/ηs</u>	<u>Volume/\AA^3</u>
PEG 400, 35 mole%	depolarized Rayleigh ^a	13.6 ± 0.8	0.12 ± 0.10	187
PEG 400, 21 mole%	depolarized Rayleigh ^a	18.6 ± 2.0	-0.09 ± 0.17	257
PEG 200, pure	depolarized Rayleigh ^a	9.25 ± 0.6	0.07 ± 0.06	128
	depolarized Rayleigh ^b	6.3 ± 0.6	-0.06 ± 0.01	
	dielectric relaxation ^c	0.91 ± 0.10	0.02 ± 0.05	
PEG 200, 35 mole%	depolarized Rayleigh ^a	13.2 ± 0.6	-0.05 ± 0.04	182
triethylene glycol, pure	depolarized Rayleigh ^b	4.6 ± 1.0	-0.06 ± 0.10	63
	dielectric relaxation ^c	1.23 ± 0.03	0.03 ± 0.01	
triethylene glycol, 35 mole%	depolarized Rayleigh ^a	8.2 ± 0.6	0.02 ± 0.02	113
diethylene glycol, pure	depolarized Rayleigh ^b	1.6 ± 0.2	0.04 ± 0.02	22
	dielectric relaxation ^c	2.25 ± 0.05	0.05 ± 0.06	
ethylene glycol, pure	depolarized Rayleigh ^b	1.4 ± 0.1	-0.01 ± 0.005	19
	dielectric relaxation ^c	2.2 ± 0.1	-0.01 ± 0.01	

a) this work

b) Ref. 11

c) Ref. 10

Figure Captions

Figure 1: Depolarized Rayleigh relaxation times as a function of T^{-1} ; note logarithmic time scale: $\blacksquare\blacksquare\blacksquare$ — — — , PEG 400, 35 mole%;
 $\square\square\square$ — — — , PEG 400, 21 mole%; $\bullet\bullet\bullet$ — — — ,
 PEG 200, pure; $\circ\circ\circ$ — — — , PEG 200, 35 mole%; $\blacktriangle\blacktriangle\blacktriangle$, triethylene glycol, pure (from Ref. 11); $\triangle\triangle\triangle$ — — — , triethylene glycol, 35 mole%.

Figure 2: Depolarized Rayleigh relaxation times as a function of η/T for pure liquids:

\blacklozenge — — — , PEG 200 (this work);
 \blacktriangle , triethylene glycol (Ref. 11);
 \blacksquare — — — , diethylene glycol (Ref. 11);
 \blacklozenge — — — , ethylene glycol (Ref. 11).

Figure 3: Depolarized Rayleigh relaxation times for PEG 400 as a function of η/T : $\bullet\bullet\bullet$ — — — , 35 mole%; $\circ\circ\circ$ — — — , 21 mole%.

Figure 4: Depolarized Rayleigh relaxation times for PEG 200 as a function of η/T :
 $\blacklozenge\blacklozenge\blacklozenge$ — — — , pure (this work); $\diamond\diamond\diamond$ — — — , 35 mole % (this work);
 \blacklozenge — — — , pure (Ref. 11).

Figure 5: Depolarized Rayleigh relaxation time for triethylene glycol as a function of η/T : $\blacktriangle\blacktriangle\blacktriangle$ — — — , pure (Ref. 11); $\triangle\triangle\triangle$ — — — , 35 mole% (this work).

Fig. 1

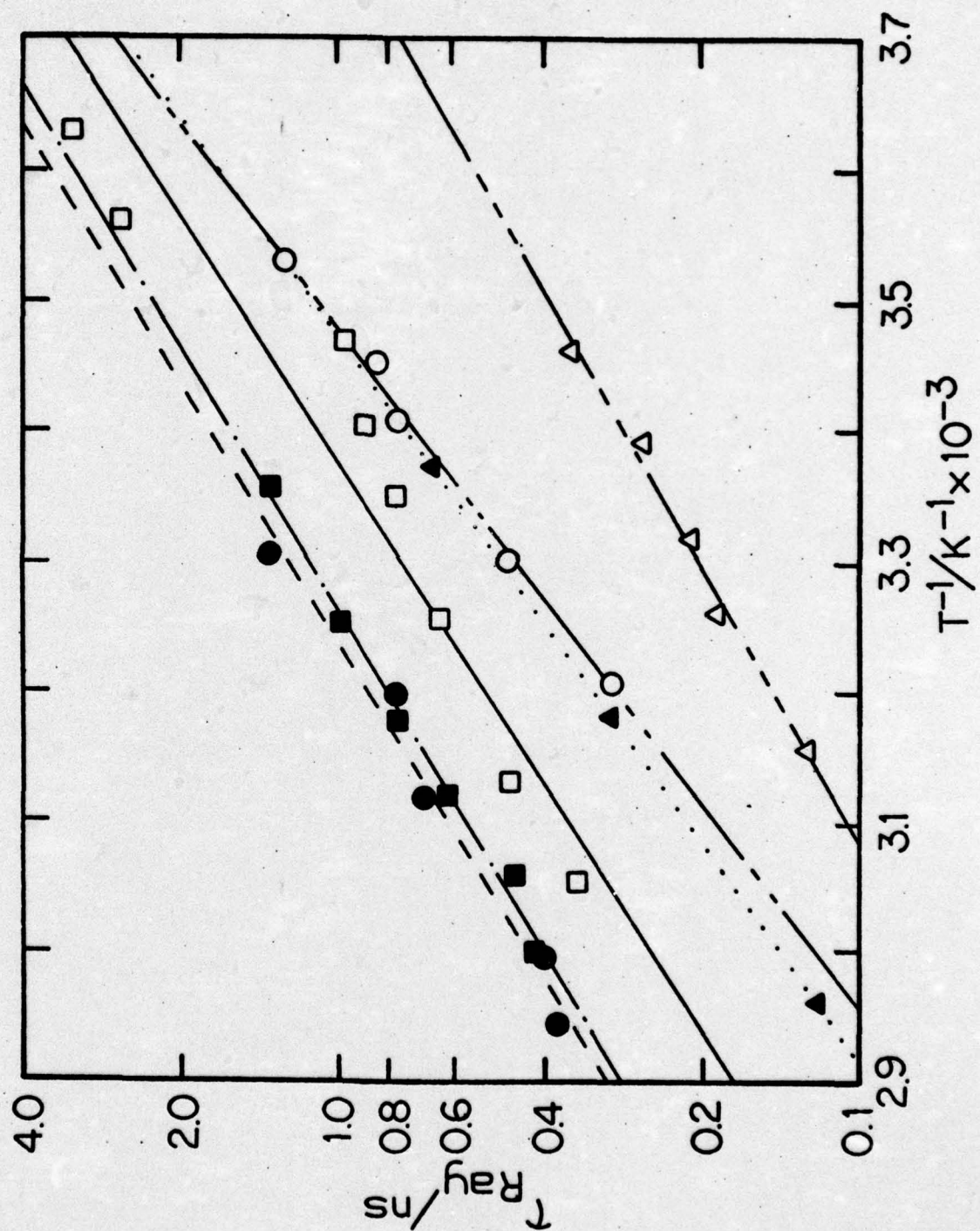


Fig. 2

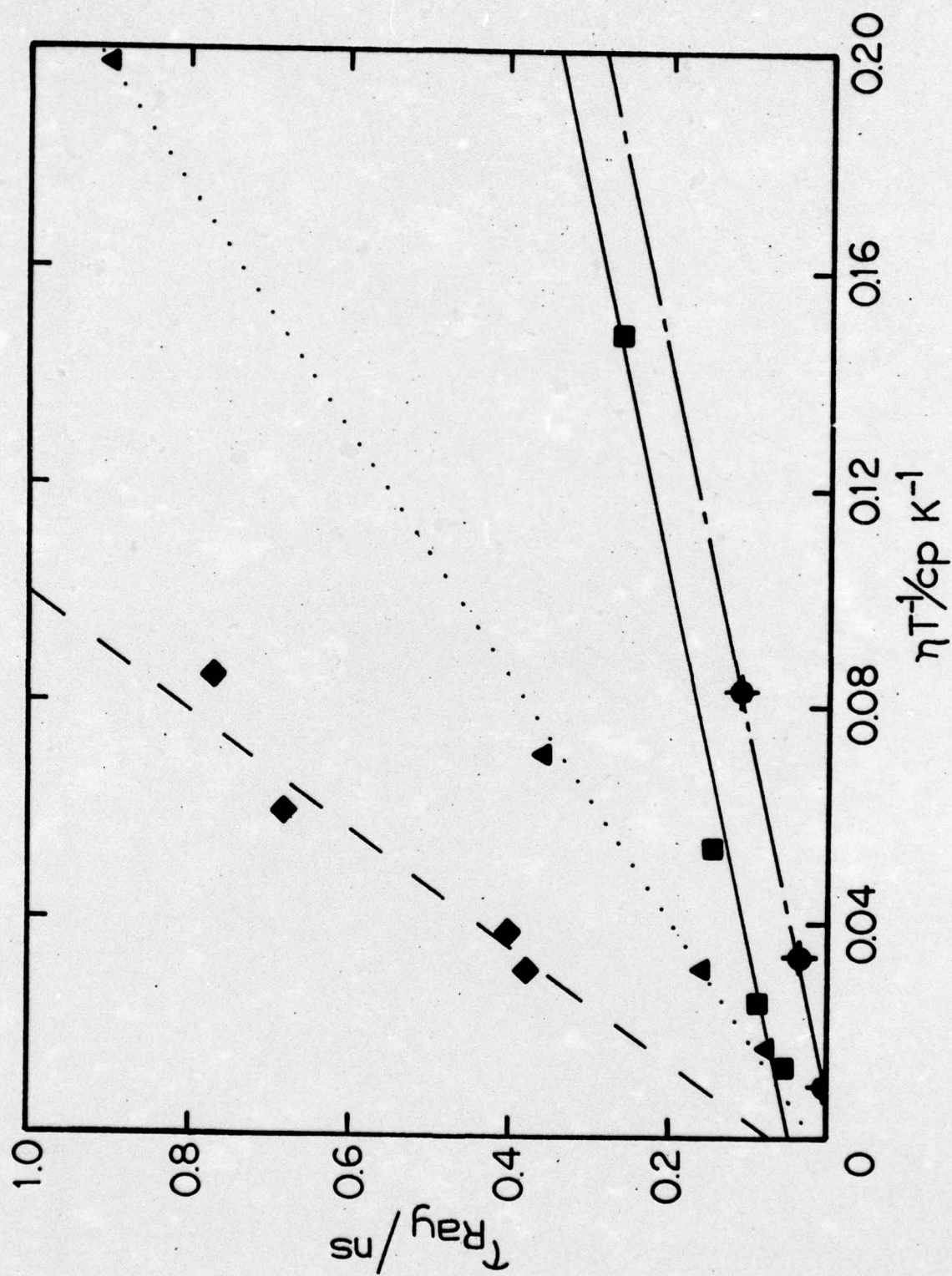


Fig. 3

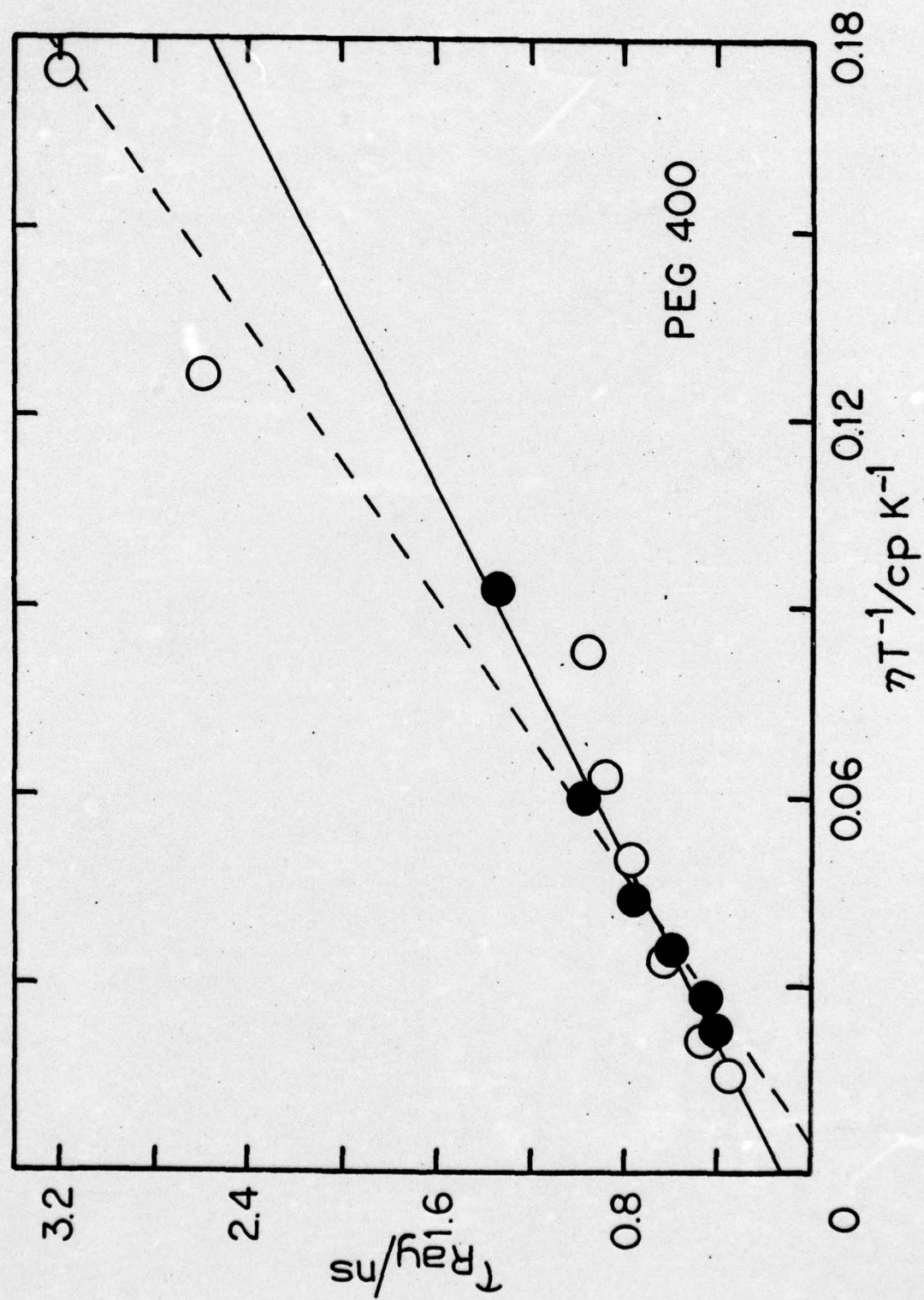


Fig. 4.

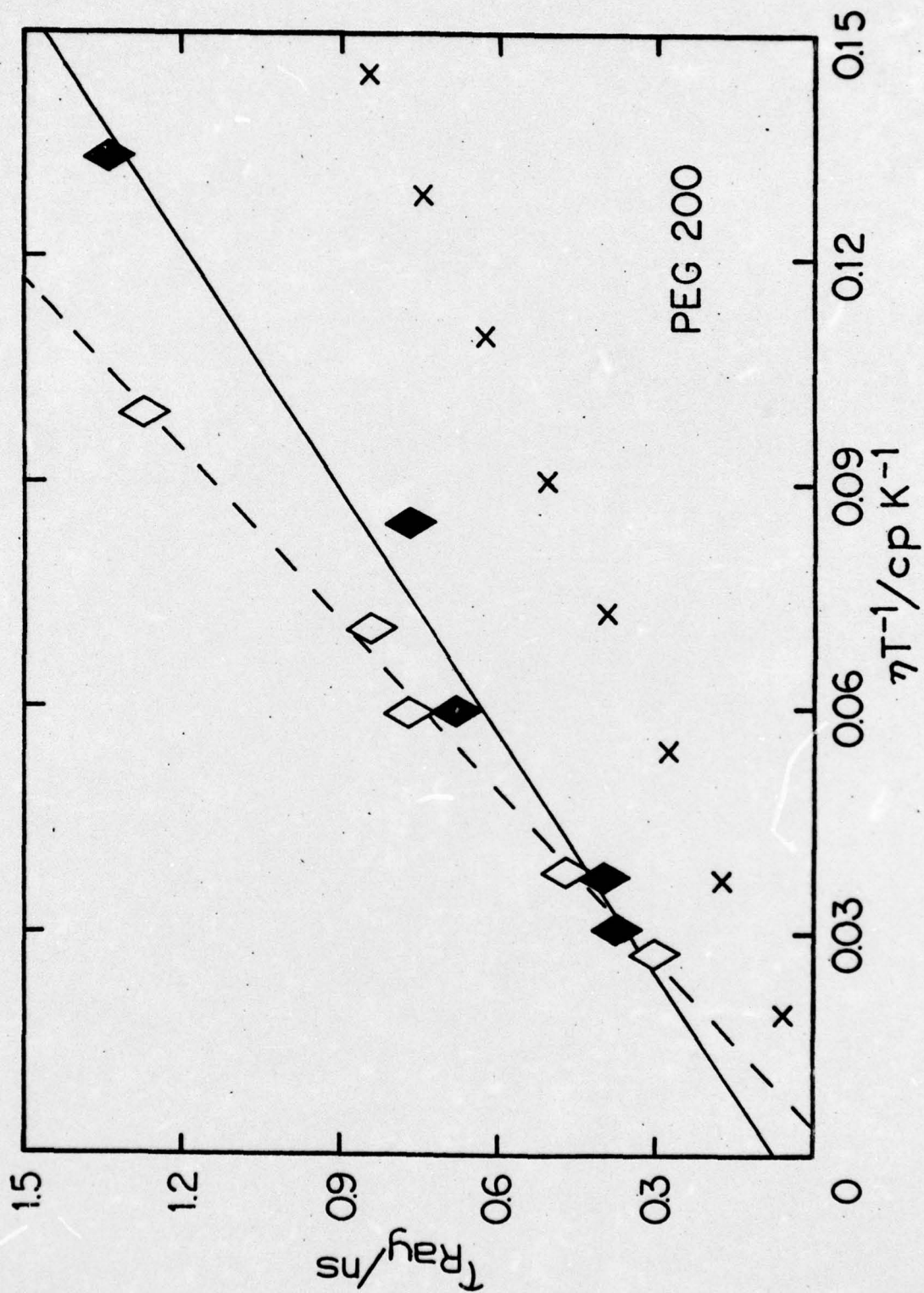
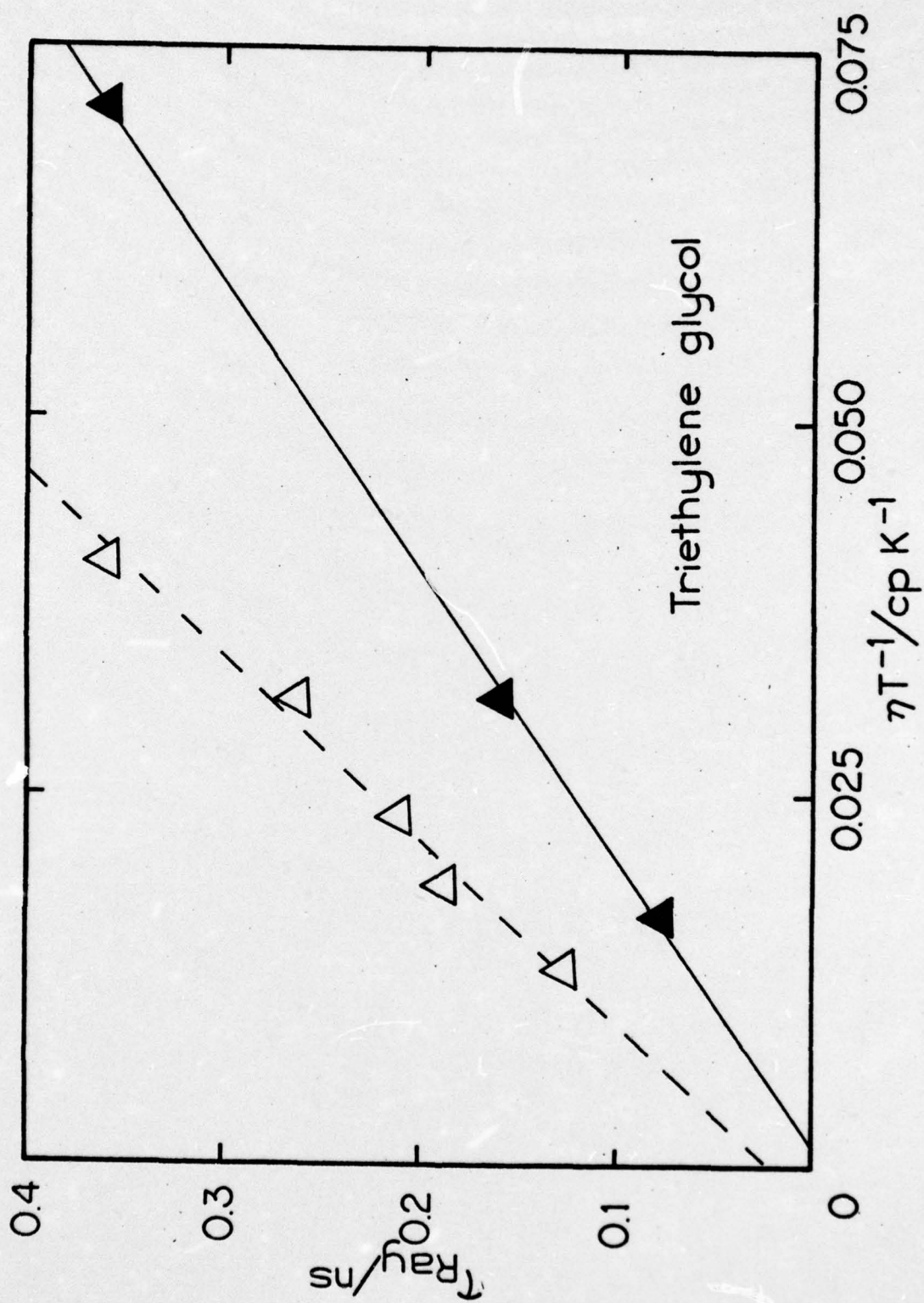


Fig 5



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